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(54) **METAL OXYHALIDE MATERIALS, THEIR USE AND METHODS FOR THEIR PRODUCTION**

METALL OXYHALOGENIDE MATERIALIEN, IHRE VERWENDUNG UND VERFAHREN ZU IHRER HERSTELLUNG

MATERIAUX D'OXYHALOGENURES METALLIQUES, LEUR UTILISATION ET LEURS PROCEDES DE PRODUCTION

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EP 0 762 995 B1

Description

[0001] This invention relates to metal oxyhalides, their use as superconductors and methods for their production.

[0002] High pressure sythesis has proved a useful technique for obtaining new, metastable copper oxide superconductors; for example, oxygen insertion into Sr_2CuO_3 at 6 GPa (Hirol, Z. et al. Nature **364,** 315 - 317 (1993)) yields superconducting $Sr_2CuO_{3,1}$, with a superconducting transition temperature (T_c) of 70 K, in which the superconducting CuO_2 layers are generated by pressure induced oxygen migration from apical to equatorial sites. Although the simple structure and high transition temperatures make this family (general formula ($Sr_{n+1}Cu_nO_{2n+1+\delta}$) of interest, the stringent synthesis conditions limit its value for applications. Metal oxide superconductors containing fluorine as an electronic dopant are per se known, for example $La_2CuO_4F_x$ is disclosed by Tissue, B. et al. in Solid St. Commun. **65**, 51 - 54 (1988), and $Nd_2CuO_{4-x}F_y$ is disclosed by James, A. et al. in Nature **338**, 240 - 241 (1989).

[0003] In JP 4-130015 copper oxide superconductive material with layered perovskite crystal structure and containing at least one of F, Cl, Br, and I are described. These compounds show the formula $(M_{1-y}A_y)_{n+1}Cu_nO_{2n+d}X_{2-d}$ in which M is at least one of Mg, Ca, Sr, Ba, and Ra, and A is at least one of Li, Na, K, and Ra or vacancy, X is at least one of F, Cl, I, and Br, n is 1 - 3, y is 0 - 5, and d is 0 - 0,6. For the preparation of these products solid powder materials of suitable carbonates, oxides and halides is mixed and heated in O_2 at 500 -900°C for 1 to 100 hours. After that the received product is ground, mixed, moulded and further heated at 500- 900 °C for 1 - 100 hours.

[0004] US 5,1081,103 describes a method of incorporating fluorine into the orthorhombic structure of the $YBa_2Cu_3O_{7-x}$ system annealing $YBa_2Cu_3O_{7-x}$ powder in a fluorine-containing gas, especially NF_2 gas or NF_3/O_2 blend of F_2N_2 blend, at a temperature of at least 250 °C, preferably higher. The operative temperature limits for the NF_3 and NF_3/O_2 treatment are 250- 300 °C, a temperature which allows sufficient reactivity with the fluorine gas while maintaining the system below temperatures at which oxygen incorporation is observed to take place. A treatment using a 10/90 % F_2/N_2 mixture showed no reaction below 500 to 550 °C.

[0005] We have discovered a novel class of metal oxyhalide materials in which the halide plays a dominant structural role, rather than merely being an electronic dopant, and which are superconductors with a maximum T_c of 46 K.

[0006] Thus, according to a first aspect of the present invention , there is provided a new method for the production of halogen-containing copper oxide of the formula $A_{n+1}Cu_nO_{2n}X_{2n+\alpha}$ where A represents one or more alkaline earth metals, X represents halogen, n is 1 or 2 and $0 < \alpha \leq 0.6$, comprising halogenating a copper oxide of the formula $A_{n+1}Cu_nO_{2n+1}$, where A and n are as defined above.

[0007] According to a second aspect of the present invention, there is provided a new method for the production of a superconductive material comprising a halogen containing copper oxide of the formula $A_{n-1}Cu_nO_{2n}X_{2n+\alpha}$ where A, X, n, and α are as defined above. Preferably, α is 0.2 to 0.5.

[0008] High pressure methods have allowed the synthesis of metastable phases (such as $YBa_2Cu_4O_8$ and $YSr_2Cu_3O_7$) which are difficult, or impossible, to obtain under ambient conditions. A recent observation relates to the oxidation of Sr_2CuO_3, the structure of which can simply be derived from that of La_2CuO_4 by removing chains of oxygen atoms from the CuO_2 layers responsible for superconductivity in doped variants such as $(La_{1-x}Sr_x)_2CuO_4$, and La_2CuO_{4+x}. At 6 GPa and 800-900°C, Sr_2CuO_3 absorbs small amounts of oxygen and transforms structurally (by oxygen transfer from apical to equatorial positions around Cu) to a metastable superconducting phase $Sr_2CuO_{3.1}$, T_c = 70 K (see Hirol et al, supra), $Sr_3Cu_2O_{5+\delta}$, the next member of this superconductor family, was reported to have T_c = 100 K (see Hirol et al, supra). Given that in both superconducting alloys and oxides the highest transition temperatures appear to occur in metastable phases, the development of alternative chemical routes to simulate the thermodynamic effects of high pressures is of fundamental importance. We have found that it is possible to insert elemental fluorine at relatively low temperatures and ambient pressure.

[0009] Thus, according to a third aspect of the present invention, there is provided a halogen-containing copper oxide of the formula $A_{n+1}Cu_nO_{2n}X_{2n+\alpha}$ where A, X, n and α are as defined above. Additionally, there is provided a superconductive material produced according to the claimed method comprising a halogen-containing copper oxide of the formula $A_{n+1}Cu_nO_{2n}X_{2n+\alpha}$, where A, X, n and α are as defined above.

[0010] Halogenation (most preferably fluorination) may be effected using a gaseous halogenating agent (eg the halogen itself) at a temperature in the range of 100 to 400°C, more preferably 150 to 250°C, and most preferably 180 to 230°C. This fluorination step has the advantage that it can be conducted at ambient pressure.

[0011] As an attractive alternative to the use of a halogen, halogenation may be effected in the solid phase using an ammonium halide (preferably ammonium fluoride or ammonium chloride) or in the gaseous or liquid phase using an organoammonium halide (eg an alkylammonium halide such as a tetraalkylammonium halide, for example tetramethyl- or tetraethyl- ammonium fluoride). Such halogenation processes may be used to advantage for the production of halogen-containing metal oxide or metal oxide carbonate superconductors generally.

[0012] Thus, according to a fourth aspect of the present invention, there is provided a method of producing a halogen-containing, metal oxide or metal oxide carbonate superconductor comprising introducing a halogen into a metal oxide or metal oxide carbonate using an ammonium halide or an organoammonium halide, eg ammonium fluoride or a

tetraalkylammonium fluoride.

[0013] In one convenient embodiment, 1 mole of Sr_2CuO_3 is reacted with 2 to 20 moles of NH_4F at 225°C for 10 hours to produce a mixture of SrF_2 and $Sr_2CuO_2F_{3+\alpha}$ with a T_c of 46K.

[0014] In another convenient embodiment, 1 mole of $(Sr_{1.5}Ba_{0.5})CuO_3$ is reacted with 2 to 20 moles of NH_4F at 225°C for 10 hours to produce a mixture of $(Sr,Ba)F_2$ and $Sr_{1.5}Ba_{0.5}Cu_2F_{2+\alpha}$ with a Tc of 60K.

[0015] In a further convenient embodiment, the cuprate carbonate $(Ba_xSr_{1-x})_2CuO_2(CO_3)$ is fluorinated using NH_4F to produce $(Ba_xSr_{1-x})_2CuO_2(CO_3)F_\alpha$, where $0 < x < 1$.

[0016] Thus, in a modification the halogen-containing copper oxide according to said first and second aspects of the present invention may also contain carbonate.

[0017] Whilst the method according to the fourth aspect of the present invention may be applied to the production of per se known halogen-containing metal oxide superconductors such as $La_2CuO_4F_x$ and $Nd_2CuO_{4-x}F_y$ noted above, it is preferably applied to the production of the novel superconductors according to said second aspect of the present invention, possibly modified by the additional presence of carbonate.

[0018] The fluorination step in the method according to said third and fourth aspects of the present invention favours production of $A_{n+1}Cu_nO_{2n}X_{2n+0.6}$. Most preferably, the material which has been subjected to halogenation is heat-treated in an inert gas atmosphere, eg nitrogen or a mixture of hydrogen and nitrogen, (without the need to use an elevated pressure) to promote loss of halide whereby to decrease the value of α until it is in the range of 0.2 to less than 0.6, preferably in the range of 0.2 to 0.5 in the case where a superconductive, halogen-containing copper oxide according to said second aspect of the present invention is required.

[0019] In one embodiment, heat treatment of $Sr_2CuO_2F_{2.6}$ in nitrogen for up to 3 hours at temperatures up to 330°C reduced the α value from 0.6 down to as low as 0.4.

[0020] In another embodiment, heat treatment of $Sr_2CuO_2F_{2.6}$ in a 10% hydrogen/nitrogen mixture for 15 minutes at temperatures up to 220°C reduced the α value from 0.6 to between 0.2 and 0.4 inclusive.

[0021] The alkaline earth metal represented by A is preferably at least one of magnesium, calcium strontium and barium, more preferably at least one of strontium and barium.

[0022] The halide represented by X is preferably fluorine or chlorine, with fluorine being more preferred.

In the accompanying drawings:-

[0023]

FIG. 1 shows powder X-ray diffraction patterns (Cu Kα1) of Sr_2CuO_3 before (top) and after (bottom) fluorination. The SrF_2 impurity is marked*

FIG. 2 shows the variation of T_c (top) and superconducting fraction (bottom) with copper oxidation state for $Sr_2CuO_2F_{2+\delta}$.

FIG. 3 shows the variation of molar susceptibility of $Sr_2CuO_2F_{2.33}$ with temperature for both field-cooled (FC) and zero field-cooled (ZFC) experiments,

FIG. 4 shows a simplified structure of $Sr_2CuO_2F_{2+\delta}$ showing idealized apical (F) and interstitial (F') sites,

FIG. 5 shows the powder X-ray diffraction pattern of fluorinated $Sr_{1.5}Ba_{0.5}CuO_2(CO_3)$, and

FIG. 6 shows the magnetic susceptibility temperature dependence of fluorinated $Sr_{1.5}Ba_{0.5}CuO_2(CO_3)$.

[0024] The present invention will now be described in further detail in the following Examples.

Example 1

[0025] Sr_2CuO_3 (prepared from $SrCO_3$ and CuO, using two heat treatments at 950°C for 16 h in air) was subjected to thermal treatments in a nickel furnace tube in a mixture of 10% F_2/90% N_2 from which traces of HF have been removed by passing over NaF. Although moderate temperatures (400°C) were found to yield predominantly SrF_2 owing to its high thermodynamic stability, at 210°C this yield of this reaction product was minimised (estimated at ~ 5 - 10% by X-ray diffraction). Upon treatment for 15 min at 210°C, a new orthorhombic (*Fmmm*) phase was formed with unit-cell dimensions implying a close structural relationship to La_4CuO_4: a = 5.394(1), b = 5.513(1), c = 13.468(3) Å (see attached Fig 1).

In one particular treatment, a 200-mg sample of Sr_2CuO_3 in a nickel boat was heated to 210°C in dry N_2 at normal ambient pressure, subjected to a flowing F_2/N_2 atmosphere for 15 min at this temperature, and allowed to cool in N_2 or air after flushing all F_2 from the system. The F content was estimated by precipitation titrations using thorium nitrate solution with methyl thymol blue indicator and comparison with standard solutions containing similar cation concentrations. Thermogravimetric analysis (H_2/N_2 mixture at 930°C to form SrF_2, SrO, Cu) followed by quantitative X-ray diffraction determination of the SrF_2:SrO ratio, provided an independent measure of the F:O ratio in the material; the Cu

oxidation state was evaluated by iodometric titration. All results were consistent with the composition $Sr_2CuC_2F_{2.6}$ (formal Cu oxidation state +2.6), which implies significant fluorine substitution for oxygen, in addition to fluorine insertion.

[0026] In view of the instability of $Sr_2CuO_2F_{2.6}$ at sintering temperatures, resistance measurements were not attempted and its superconducting properties were examined magnetically with a d.c. SQUID magnetometer, using a field of 10^{-3} T. Some samples were superconducting but with small (< 1%) superconducting volume fractions; low temperature reductions resulted in fluorine loss to give $Sr_2CuO_2F_{2+\alpha}$ with improved superconducting properties. Samples where therefore annealed for up to 3h in N_2 (temperatures up to 330°C, $0.4 \leq \alpha \leq 0.6$) or for 15 min in a 10% H_2/N_2 mixture (temperatures up to 220°C, $0.2 \leq \alpha \leq 0.4$). The superconducting properties (T_c and percentage flux expulsion) are shown in attached Fig 2 in relation to the Cu oxidation state, and the susceptibility for the sample with T_c = 46 K is shown in attached Fig 3. The calculated superconducting volume fractions are small for all samples; this is attributed to particle size effects as it is well established that the magnetization is reduced for powders comprising crystallites with dimensions comparable to the London penetration depth. This interpretation is supported by the broad X-ray diffraction peaks for $Sr_2CuO_2F_{2.6}$ (Fig 1), which indicate a mean crystallite size of only ~700A, and the small divergence between field-cooled and zero field-cooled susceptibilities (Fig 3). The data in Fig 2 suggests that T_c and the superconducting volume fraction may show a broad maximum at a formal Cu oxidation state of +2.2 to +2.3, which is similar to other copper oxide superconductors. The wide range of oxidation states for which superconductivity is observed is thought to reflect composition variations, which are to be expected due to the low temperatures of the synthesis conditions.

[0027] Although neither X-ray nor neutron diffraction can differentiate O and F ions, bulk structural characteristics were investigated using powder neutron diffraction data (collected on a 4-g sample using the POLARIS diffractometer, Isis Rutherford Appleton Laboratory) to aid accurate location of the light atoms. Although structure refinement based on a simple La_2CuO_4 - type model produced an unacceptably high and anisotropic temperature factor for the apical anions (B_{11} = 6Å^2, B_{22} = 23Å^2, B_{33} = 0Å^2) when considered as a single site, splitting this site into two positions was more satisfactory and resulted in sensible isotropic thermal parameters. This feature is similar to that observed in $La_2CuO_{4+\delta}$ (see Chaillot, C. et al, Physics C**159**, 183 (1989) and Radaell, et al Phys. Rv. B**48**,499 (1993)) and suggests the presence of interstitial F ions, consistent with the formula $Sr_2CuO_2F_{2+\alpha}$. Inclusion of such ions near the ideal/(¼, /¼, 1¼) position produced a stable refinement, and the results are shown in Table 1 below. The interstitial F (F(3)), which would have four unacceptably short contacts (~2.15Å) to neighbouring F ions in an undistorted structure, seems to be displaced away from three neighbours towards the fourth, which subsequently shifts by ~0.6Å to the F(2) site. In this way, four satisfactory F-F distances are achieved (Table 1). Although the defect model is slightly different from those proposed for $La_2CuO_{4-\delta}$, one of which involves a very short O-O distance, it is chemically plausible and avoids all close F-F contacts. In accordance with this model, the F(3) and F(2) occupancies were constrained to be equal in the final refinement, which suggested the composition $Sr_2CuO_2F_{2.57}$, in excellent agreement with analysis. Bond valence sum calculations suggested a Cu oxidation state of 2.23 (using Cu^{2+} values for r_0 -see Brown, I et al Acta Crystallogr. **B41**, 244-247 (1985)), which is lower than the expected value of +2.6. Madelung energies were calculated for different distributions of O and F atoms in the parent $Sr_2CuO_2F_2$, and indicated a substantial preference for apical F (11,072 kJmol^{-1}) rather than equatorial F (10,138 kJmol^{-1}) and provided strong support for the presence of only apical F. The structure of $Sr_2CuO_2F_{2.6}$ is shown in simplified form in Fig 4.

[0028] The evidence that F avoids the equatorial sites clearly demonstrates the potential role of oxy-fluorides for forming new high temperature copper oxide superconductors; superconductivity in $Sr_2CuO_2F_2$ has been induced by incorporating interstitial F. The partial replacement of the apical F ions by O^{2-} could provide an alternative means of an ionic chemical control of the electron carrier density, in analogous fashion to Sr and Ba substitutions for La in La_3CuO_4. Of greater significance is the demonstration that the F site preference can promote interchange of O and F ions to create the structural features necessary to support superconductivity in phases which are otherwise unsuited, for example, Sr_2CuO_3.

TABLE 1

Refined structural data for $Sr_2CuO_2F_{2.6}$						
Atom	Position	x	y	z	B(Å^2)	Cell occupancy
Sr	8i	0	0	0.3680(1)	0.67(2)	8
Cu	4a	0	0	0	0.66(3)	4
0	8e	0.25	0.25	0	0.76(3)	8
F(1)	32p	0.0358(8)	0.0483(7)	0.1802(4)	0.67(7)	5.72(5)
F(2)	32p	0.059	0.151(2)	0.1802(4)	0.67(7)	2.28(5)
F(3)	32p	0.196(2)	0.239(2)	0.2212(8)	0.67(7)	2.28(5)

[0029] Unit cell dimensions a = 5.394(1)Å, b = 5.513(1)Å, c = 13.468(3)Å; space group Fmmm; R factors; R_{wp} = 3.7%, R_{exp} = 1.2%, R_I= 7.2%. Bond distances (Å): Cu-O, 1.928(1) [x4]; Cu-F(1), 2.45(1); Cu-O/F(2), 2.59(1); F(3)-F (1); 2..50(3). 2.65(3), 2.56(3); F(3)-F(2), 2.55(3).

Example 2

[0030] 1 mmol of $Sr_{1.5}Ba_{0.5}CuO_2(CO_3)$ (having a $(Ba_xSr_{1-x})_2CuO_2(CO_3)$ structure) was intimately ground with 0.5 mmol of NH_4F and the resultant brown coloured mixture was then heated in air for 12 hours at 200°C to produce a black powder. Such black powder was characterised by both X-ray diffraction (PXD) and magnetic susceptibility measurements. PXD confirmed that this new material retained the $(Ba_xSr_{1-x})_2CuO_2(CO_3)$ structure, but gave no information as to the location of the fluorine (see Fig. 5). The magnetic susceptibility measurements showed the presence of a superconducting transition at a temperature of about 55 K (see Fig. 6). Although the location of the fluorine has not yet been established, it is possible to envisage that fluorine insertion occurs in the carbonate layer, thus doping the CuO_2 planes. The resulting structure could therefore be described as $(Ba_xSr_{1-x})_2CuO_2(CO_3)F\alpha$.

Claims

1. A method of producing a halogen-containing copper oxide of the formula $A_{n+1}Cu_nO_{2n}X_{2n+\alpha}$ where A represents one or more alkaline earth metals, X represents halogen, n is 1 or 2 and $0 < \alpha \leq 0.6$, comprising the step of halogenating a copper oxide of the formula $A_{n+1}Cu_nC_{2n+1}$,
   wherein the halogenating step is effected at a temperature in the range of 150 to 250 °C, and if necessary comprising a heat treatment in an inert gas atmosphere to promote loss of halide whereby to decrease the value of α until it is in the range 0.2 to less than 0.6.

2. A method as claimed in claim 1, wherein the halogenating step is a fluorinating step.

3. A method as claimed in claim 1 or 2, wherein the halogenating step is effected using a gaseous halogenating agent.

4. A method as claimed in claim 3, wherein the halogenating agent is the halogen.

5. A method as claimed in claim 1, 2, 3 or 4, wherein the halogenating step is effected at a temperature in the range of 180 to 230 °C.

6. A method as claimed in any one of claims 1 to 5, wherein the halogenating step is effected at ambient pressure.

7. A method as claimed in claim 1 or 2, wherein the halogenating step is effected in the solid phase using an ammonium halide or in the gaseous or liquid phase using an organoammonium halide.

8. A method of producing a halogen-containing metal oxide or metal oxide carbonate superconductor, comprising the step of introducing a halogen into a metal oxide or metal oxide carbonate at a temperature in the range of 150 to 250 °C, preferably in the range of 180 to 230°C, using an ammonium halide or an organoammonium halide.

9. A method as claimed in claim 8, wherein the ammonium halide is ammonium fluoride.

10. A method as claimed in claim 8, wherein the organoammonium halide is a tetraalkylammonium fluoride.

11. A method as claimed in claim 1 or 8, wherein 1 mole of Sr_2CuO_3 is reacted with 2 to 20 moles of NH_4F at 225 °C for 10 hours to produce a mixture of SrF_2 and $Sr_2CuO_2F_{2+\alpha}$ with a T_c of 46 K.

12. A method as claimed in claim 1 or 8, wherein 1 mole of $(Sr_{1,5}Ba_{0,5})CuO_3$ is reacted with 2 to 20 moles of NH_4F at 225 °C for 10 hours to produce a mixture of (Sr, Ba)F_2 and $Sr_{1,5}Ba_{0,5}CuO_2F_{2+\alpha}$ with a T_c of 60 K.

13. A method as claimed in claim 8, wherein the copper oxide carbonate $(Ba_xSr_{1-x})_2CuO_2(CO_3)$ is fluorinated using NH_4F to produce $(Ba_xSr_{1-x})_2CuO_2(CO_3)F_\alpha$, where $0 < x < 1$, and $0 < \alpha \leq 0.6$

14. A halogen-containing copper oxide of the formula $A_{n+1}Cu_nO_{2n}X_{2n+\alpha}$ where A represents one or more alkaline earth metals, X represents halogen, n is 1 or 2 and $0 < \alpha \leq 0.6$ prepared by a method as claimed in claims 1 to 10.

15. A halogen-containing copper oxide as claimed in claim 14, wherein α is 0.2 to 0.5.

16. A superconductive material produced according to a method as claimed in claims 1 to 10 comprising a halogen-containing copper oxide of the formula $A_{n+1}Cu_nO_{2n}X_{2n+\alpha}$, where A, X, n and α are as defined in claim 14 or 15.

17. Halogen-containing copper oxide or halogen-containing copper oxide carbonate prepared by a method as claimed in claims 8 to 13.

18. A method as claimed in claim 1 or 8, wherein the material which has been subjected to halogenation is heat-treated in an inert gas atmosphere to promote loss of halide whereby to decrease the value of α until it is in the range of 0.2 to 0.5 in the case where a superconductive, halogen-containing copper oxide according to claim 16.

19. A method as claimed in claim 18, wherein heat treatment of $Sr_2CuO_2F_{2.6}$ is effected in nitrogen for up to 3 hours at temperatures up to 330 °C to reduce the α value from 0.6 down to 0.4.

20. A method as claimed in claim 18, wherein heat treatment of $Sr_2CuO_2F_{2.6}$ is effected in a 10% hydrogen/nitrogen mixture for 15 minutes at temperatures up to 220 °C to reduce the α value from 0.6 to between 0.2 and 0.4 inclusive.

Patentansprüche

1. Verfahren zur Herstellung eines halogenhaltigen Kupferoxids der Formel $A_{n+1}Cu_nO_{2n}X_{2n+\alpha}$, worin A für ein oder mehrere Erdalkalimetalle steht, X für Halogen steht, n gleich 1 oder 2 und $0 < \alpha \leq 0{,}6$ ist, bei dem man ein Kupferoxid der Formel $A_{n+1}Cu_nO_{2n+1}$ bei einer Temperatur im Bereich von 150 bis 250°C halogeniert und gegebenenfalls eine Wärmebehandlung in einer Inertgasatmosphäre zur Förderung von Halogenidverlust durchführt und dadurch den Wert von α verringert, bis er im Bereich von 0,2 bis weniger als 0,6 liegt.

2. Verfahren nach Anspruch 1, bei dem es sich bei der Halogenierung um eine Fluorierung handelt.

3. Verfahren nach Anspruch 1 oder 2, bei dem man die Halogenierung mit einem gasförmigen Halogenierungsmittel durchführt.

4. Verfahren nach Anspruch 3, bei dem man als Halogenierungsmittel das Halogen verwendet.

5. Verfahren nach Anspruch 1, 2, 3 oder 4, bei dem man die Halogenierung bei einer Temperatur im Bereich von 180 bis 230°C durchführt.

6. Verfahren nach einem der Ansprüche 1 bis 5, bei dem man die Halogenierung bei Normaldruck durchführt.

7. Verfahren nach Anspruch 1 oder 2, bei dem man die Halogenierung in fester Phase mit einem Ammoniumhalogenid oder in gasförmiger oder flüssiger Phase mit einem Organoammoniumhalogenid durchführt.

8. Verfahren zur Herstellung eines halogenhaltigen Metalloxid- oder Metalloxidcarbonat-Supraleiters, bei dem man bei einer Temperatur im Bereich von 150 bis 250°C, vorzugsweise im Bereich von 180 bis 230°C, unter Verwendung eines Ammoniumhalogenids oder eines Organoammoniumhalogenids in ein Metalloxid oder Metalloxidcarbonat ein Halogen einführt.

9. Verfahren nach Anspruch 8, bei dem man als Ammoniumhalogenid Ammoniumfluorid verwendet.

10. Verfahren nach Anspruch 8, bei dem man als Organoammoniumhalogenid Tetraalkylammoniumfluorid verwendet.

11. Verfahren nach Anspruch 1 oder 8, bei dem man 1 mol Sr_2CuO_3 mit 2 bis 20 mol NH_4F bei 225°C über einen Zeitraum von 10 Stunden zu einer Mischung von SrF_2 und $Sr_2CuO_2F_{2+\alpha}$ mit einer T_c von 46 K umsetzt.

12. Verfahren nach Anspruch 1 oder 8, bei dem man 1 mol $(Sr_{1,5}Ba_{0,5})CuO_3$ mit 2 bis 20 mol NH_4F bei 225°C über einen Zeitraum von 10 Stunden zu einer Mischung von $(Sr,Ba)F_2$ und $Sr_{1,5}Ba_{0,5}CuO_2F_{2+\alpha}$ mit einer T_c von 60 K umsetzt.

13. Verfahren nach Anspruch 8, bei dem man das Kupferoxidcarbonat $(Ba_xSr_{1-x})_2CuO_2(CO_3)$ mit NH_4F fluoriert, wobei man $(Ba_xSr_{1-x})_2CuO_2(CO_3)F_\alpha$ mit $0 < x < 1$ und $0 < \alpha \leq 0,6$ erhält.

14. Halogenhaltiges Kupferoxid der Formel $A_{n+1}Cu_nO_{2n}X_{2n+\alpha}$, worin A für ein oder mehrere Erdalkalimetalle steht, X für Halogen steht, n gleich 1 oder 2 und $0 < \alpha \leq 0,6$ ist, das nach einem Verfahren nach einem der Ansprüche 1 bis 10 hergestellt worden ist.

15. Halogenhaltiges Kupferoxid nach Anspruch 14, worin α einen Wert von 0,2 bis 0,5 aufweist.

16. Supraleitendes Material, das nach einem Verfahren nach einem der Ansprüche 1 bis 10 hergestellt worden ist und ein halogenhaltiges Kupferoxid der Formel $A_{n+1}Cu_nO_{2n}X_{2n+\alpha}$, worin A, X, n und α die in Anspruch 14 oder 15 angegebene Bedeutung haben, enthält.

17. Halogenhaltiges Kupferoxid oder halogenhaltiges Kupferoxidcarbonat, das nach einem Verfahren nach einem der Ansprüche 8 bis 13 hergestellt worden ist.

18. Verfahren nach Anspruch 1 oder 8, bei dem man in dem Fall, daß ein supraleitendes, halogenhaltiges Kupferoxid nach Anspruch 16 gefordert ist, das der Halogenierung unterworfene Material in einer Inertgasatmosphäre zur Förderung von Halogenidverlust wärmebehandelt und dadurch den Wert von α verringert, bis er im Bereich von 0,2 bis 0,5 liegt.

19. Verfahren nach Anspruch 18, bei dem man $Sr_2CuO_2F_{2,6}$ in Stickstoff über einen Zeitraum von bis zu 3 Stunden bei Temperaturen bis zu 330°C wärmebehandelt und dadurch den α-Wert von 0,6 auf 0,4 verringert.

20. Verfahren nach Anspruch 18, bei dem man $Sr_2CuO_2F_{2,6}$ in einem Gemisch aus 10% Wasserstoff und Stickstoff über einen Zeitraum von 15 Minuten bei Temperaturen bis zu 220°C wärmebehandelt und dadurch den α-Wert von 0,6 auf einen Wert zwischen 0,2 und 0,4 inklusive verringert.

Revendications

1. Procédé de production d'un oxyde de cuivre contenant de l'halogène de formule $A_{n+1}\,Cu_n\,O_{2n}\,X_{2n+\alpha}$, dans laquelle A représente un ou plusieurs métaux alcalino-terreux, X représente de l'halogène, n est 1 ou 2 et $0 < \alpha \leq 0,6$, comprenant l'étape consistant à halogéner un oxyde de cuivre de formule $A_{n+1}\,Cu_n\,O_{2n+1}$, dans lequel l'étape d'halogénation est effectuée à une température comprise dans la gamme allant de 150 à 250°C, et si nécessaire, comprenant un traitement thermique dans une atmosphère de gaz inerte afin de promouvoir la perte d'halogénure et ainsi abaisser la valeur de α jusqu'à ce que celle-ci soit dans la gamme allant de 0,2 à moins de 0,6.

2. Procédé selon la revendication 1, dans lequel l'étape d'halogénation est une étape de fluoration.

3. Procédé selon la revendication 1 ou 2, dans laquelle l'étape d'halogénation est effectuée en utilisant un agent halogénant gazeux.

4. Procédé selon la revendication 3, dans lequel l'agent halogénant est l'halogène.

5. Procédé selon la revendication 1, 2, 3 ou 4, dans lequel l'étape d'halogénation est effectuée à une température comprise dans la gamme allant de 180 à 230°C.

6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel l'étape d'halogénation est effectuée à la pression ambiante.

7. Procédé selon la revendication 1 ou 2, dans lequel l'étape d'halogénation est effectuée en phase solide en utilisant un halogénure d'aluminium, ou en phase liquide ou gazeuse en utilisant un halogénure d'organoammonium.

8. Procédé de production d'un oxyde métallique contenant de l'halogène ou d'un supraconducteur carbonate d'oxyde métallique, comprenant l'étape consistant à introduire un halogène dans un oxyde métallique ou un carbonate d'oxyde métallique à une température comprise dans la gamme allant de 150 à 250°C, de préférence dans la gamme allant de 180 à 230°C, en utilisant un halogénure d'ammonium ou un halogénure d'organoammonium.

9. Procédé selon la revendication 8, dans lequel l'halogénure d'ammonium est du fluorure d'ammonium.

10. Procédé selon la revendication 8, dans lequel l'halogénure d'organoammonium est du fluorure de tétraalkylammonium.

11. Procédé selon la revendication 1 ou 8, dans lequel 1 mole de Sr_2CuO_3 est mise à réagir avec de 2 à 20 moles de NH_4F à 225°C pendant 10 heures afin de produire un mélange de SrF_2 et $Sr_2CuO_2F_{2+\alpha}$ avec une valeur Tc de 46 K.

12. Procédé selon la revendication 1 ou 8, dans lequel une mole de $(Sr_{1,5}Ba_{0,5})CuO_3$ est mise à réagir avec de 2 à 20 moles de NH_4F à 225°C pendant 10 heures pour produire un mélange de (Sr, Ba)F_2 et $Sr_{1,5}Ba_{0,5}CuO_2F_{2+\alpha}$, avec une valeur Tc de 60 K.

13. Procédé selon la revendication 8, dans lequel le carbonate d'oxyde de cuivre $(Ba_xSr_{1-x})_2CuO_2(CO_3)$ est fluoré en utilisant du NH_4F pour produire $(Ba_xSr_{1-x})_2CuO_2(CO_3)F_\alpha$, dans lequel $0 < x < 1$ et $0 < \alpha \leq 0,6$.

14. Oxyde de cuivre contenant de l'halogène de formule $A_{n+1}Cu_nO_{2n}X_{2n+\alpha}$, dans laquelle A représente un ou plusieurs métaux alcalino-terreux, X représente l'halogène, n est 1 ou 2 et $0 < \alpha \leq 0,6$, préparé par un procédé selon les revendications 1 à 10.

15. Oxyde de cuivre contenant de l'halogène selon la revendication 14, dans lequel a est 0,2 à 0,5.

16. Matériau supraconducteur produit par un procédé selon les revendications 1 à 10, comprenant un oxyde de cuivre contenant de l'halogène de formule $A_{n+1}Cu_nO_{2n}X_{2n+\alpha}$, dans laquelle A, X, n et α sont comme défini dans la revendication 14 ou 15.

17. Oxyde de cuivre contenant de l'halogène ou carbonate d'oxyde de cuivre contenant de l'halogène préparé par un procédé selon les revendications 8 à 13.

18. Procédé selon la revendication 1 ou 8, dans lequel le matériau qui a été soumis à l'halogénation est traité thermiquement dans une atmosphère de gaz inerte afin de promouvoir la perte d'halogénure, et ainsi abaisser la valeur de a jusqu'à ce que celle-ci soit dans la gamme allant de 0,2 à 0,5 dans le cas d'un oxyde de cuivre contenant de l'halogène supraconducteur selon la revendication 16.

19. Procédé selon la revendication 18, dans lequel le traitement thermique de $Sr_2CuO_2F_{2,6}$ est effectué dans de l'azote pendant jusqu'à 3 heures à des températures allant jusqu'à 330°C afin d'abaisser la valeur de α de 0,6 jusqu'à 0,4.

20. Procédé selon la revendication 18, dans lequel le traitement thermique de $Sr_2CuO_2F_{2,6}$ est effectué dans un mélange d'hydrogène à 10% d'azote pendant 15 minutes à des températures allant jusqu'à 220°C afin de réduire la valeur de α de 0,6 à entre 0,2 et 0,4 inclus.

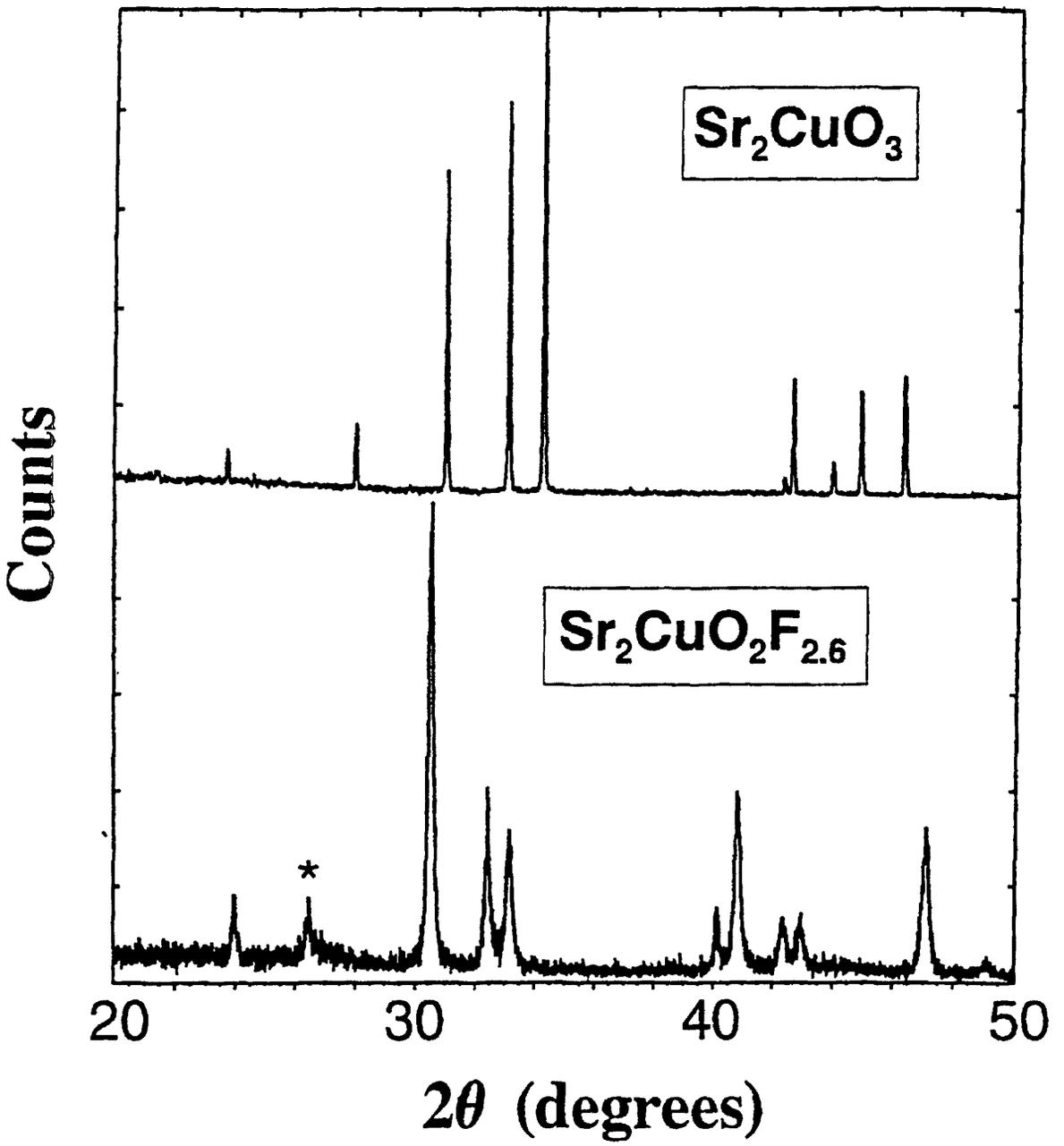


FIG 1

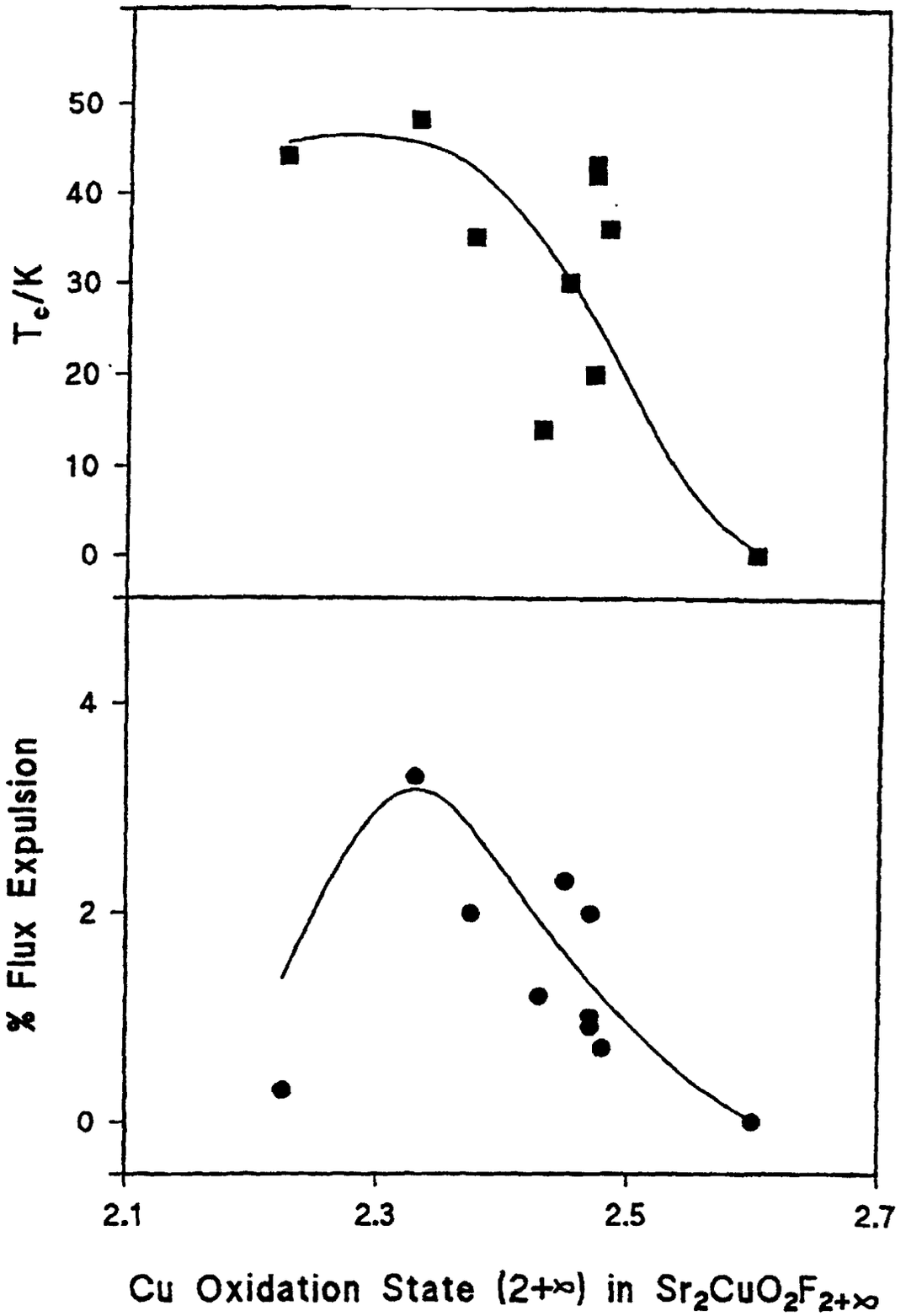

50
40
30
20
10
0
T_c/K
4
2
0
% Flux Expulsion
2.1
2.3
2.5
2.7
Cu Oxidation State (2+∞) in $Sr_2CuO_2F_{2+\infty}$

FIG 2

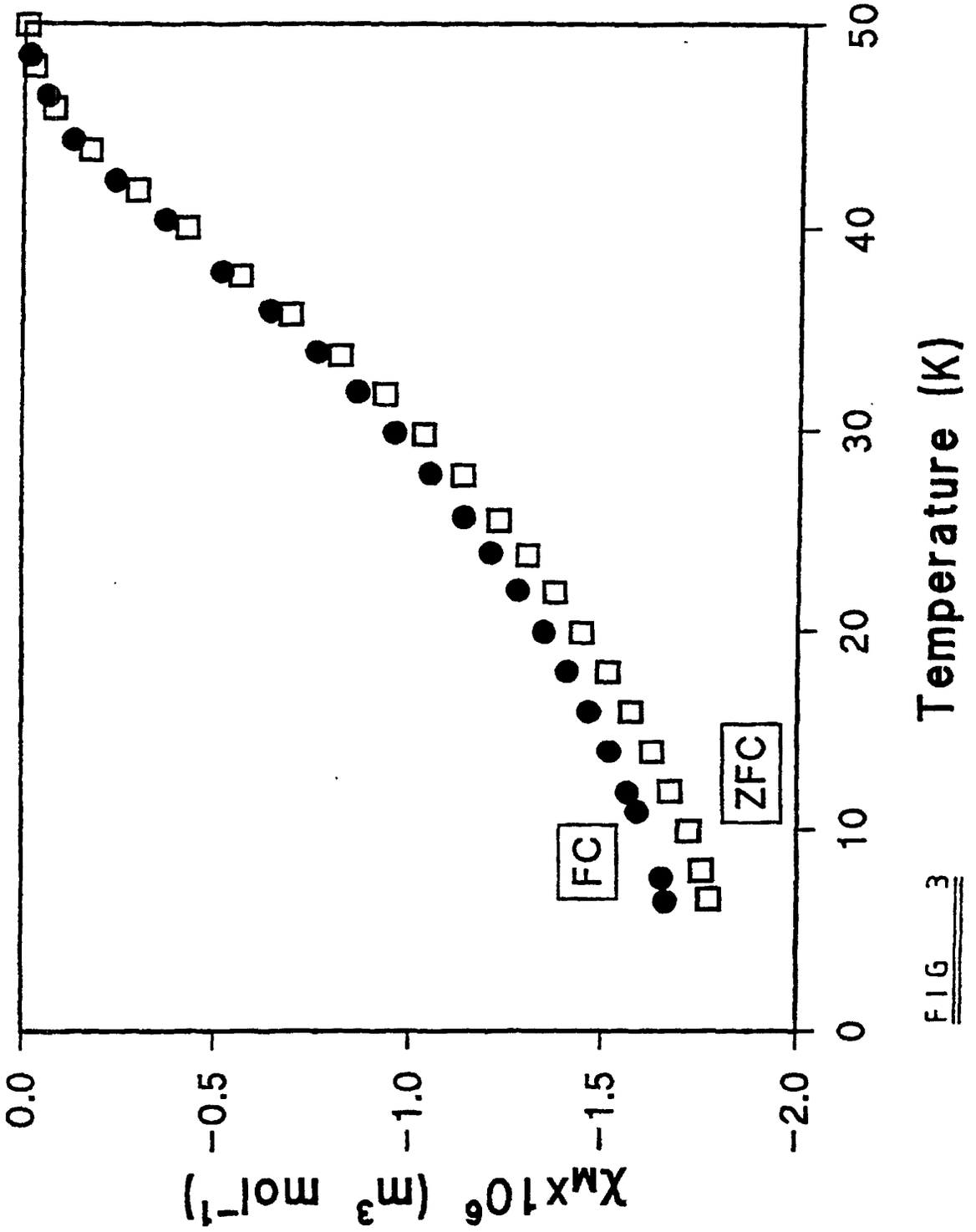

0.0
−0.5
−1.0
−1.5
−2.0
$\chi_M x10^6$ (m^3 mol^{-1})
0
10
20
30
40
50
Temperature (K)
FC
ZFC

FIG 3

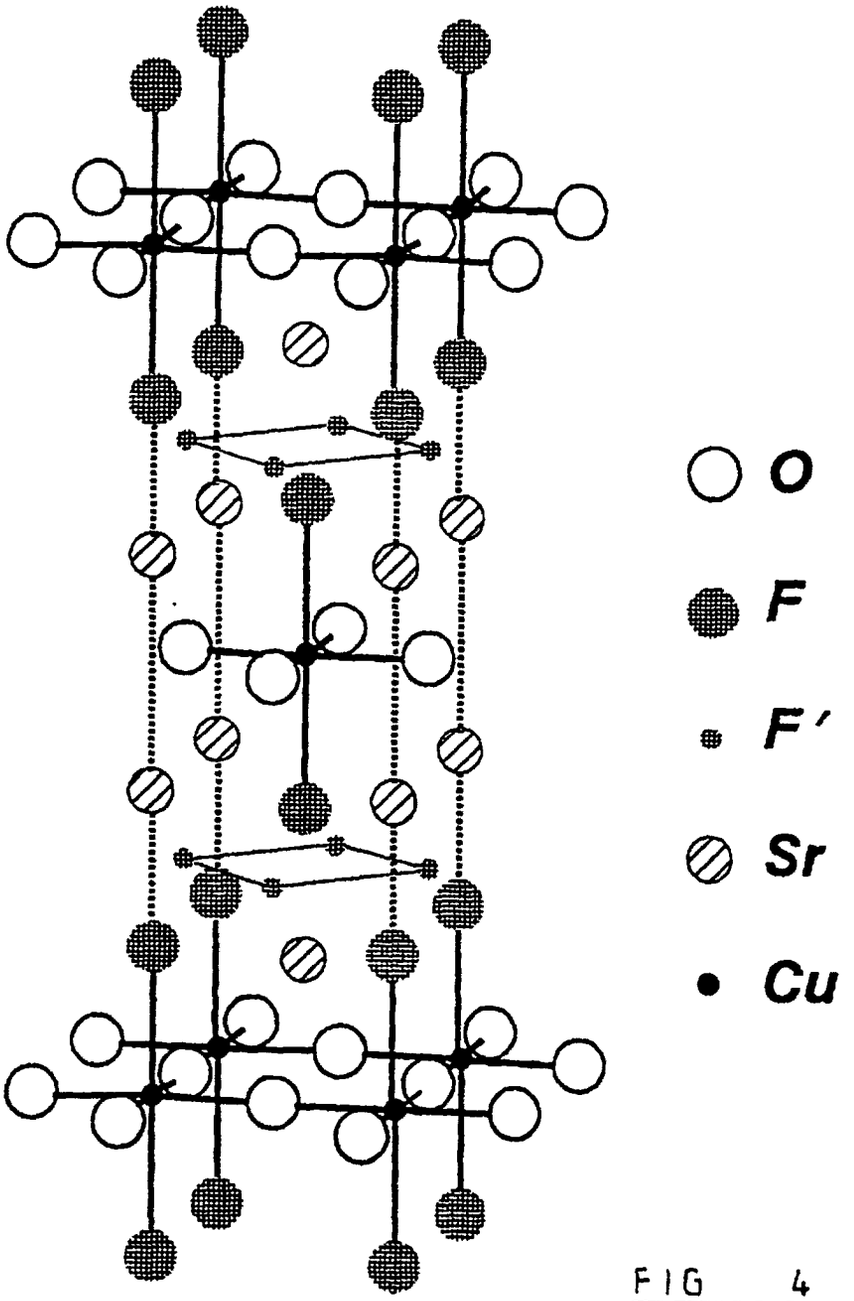


FIG 4

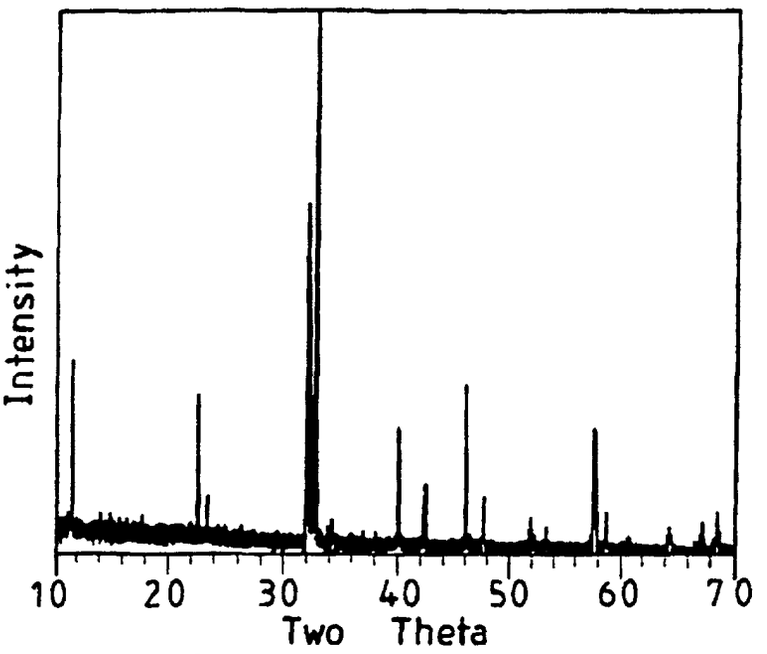
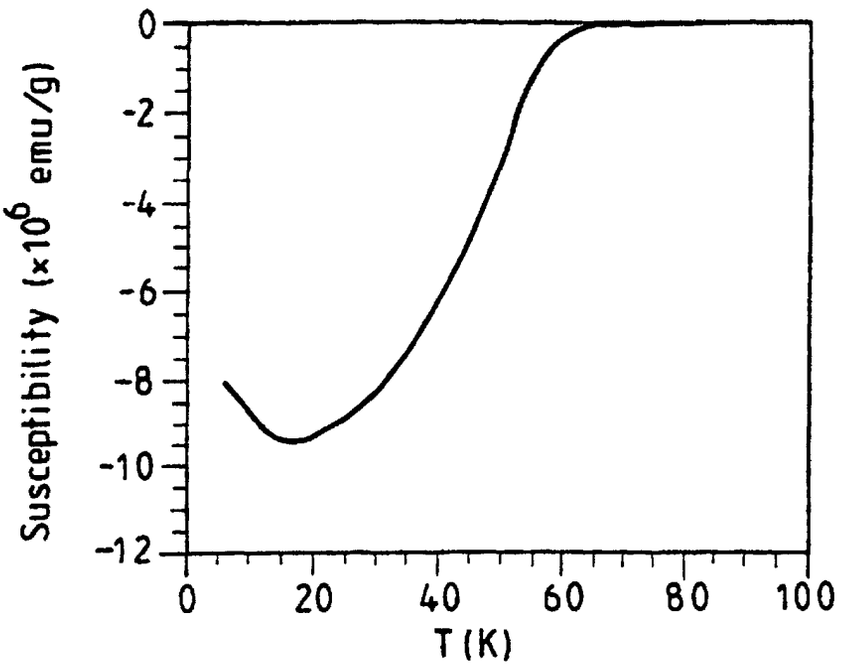

Intensity
10
20
30
40
50
60
70
Two Theta

FIG 5


Susceptibility (×10⁶ emu/g)
0
-2
-4
-6
-8
-10
-12
0
20
40
60
80
100
T (K)